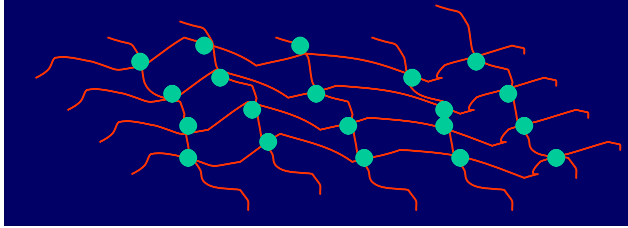
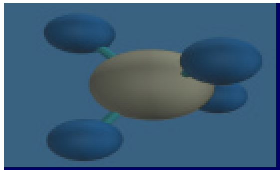
Polymer Systems and Film Formation Mechanisms in High Solids, Powder, and UV Cure Systems

J. Baghdachi, Ph.D.
Coatings Research Institute
Eastern Michigan University
(734) 487-3192
Freshpaint@aol.com
jamil.baghdachi@emich.edu

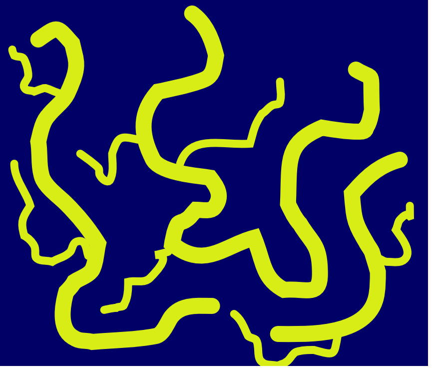


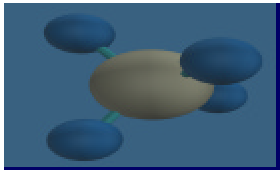


Film Formation in Coatings

Outline:

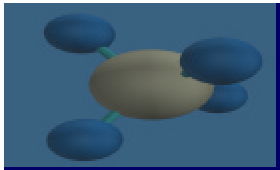
- Thermoplastic systems
- Thermosetting systems
- Variables controlling property development
- Stages of property development
- Waterborne
- Energy cure
- Powder coating





Film Formation

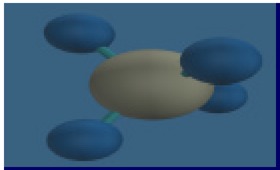
Almost all desirable properties of a coating film strongly depend upon the quality and integrity of the coating film which in turn depends upon the polymer chemistry, formulation variables, the T_g of the dry film and the surface characteristics of the substrate among other factors.



Film Formation

Coating properties influenced by film formation process

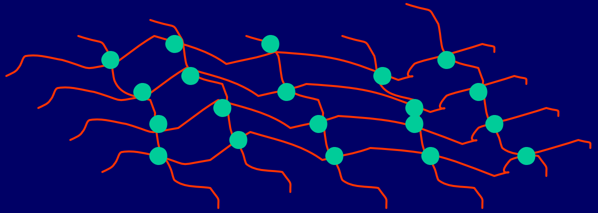
Adhesion
Chemical resistance
Mechanical properties
Dirt pick up
Flow
Gloss
Pop (blister)
Sag
Surface dry and hardness development



Film Formation

Three major classification of film formers

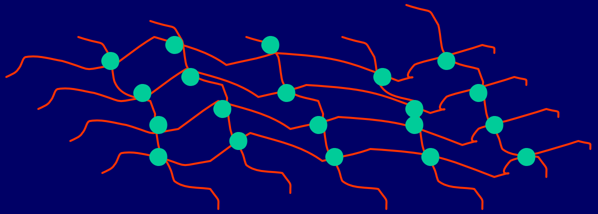
- Thermoplastic materials
- Chemically converting systems
- Latex systems

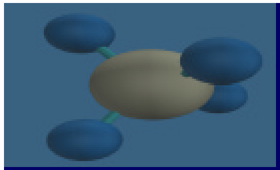


Film Formation

Chemical and Physical Variables Controlling Property Development

Molecular weight
Crosslink Density
Glass Transition Temperature
Building blocks
Viscosity
Cure Temperature
Formulation variables





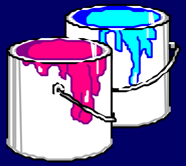
Film Formation

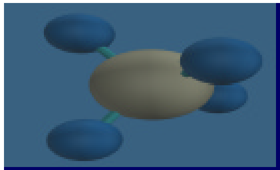
Property	Thermoplastic	Thermoset
MW prior to application	High	Low
MW as dry film	High	Very high
Crosslink density	Very low	Moderate-v.high
Hardness	Poor-good	Moderate-Excellent
Solvent resistance	Poor-good	Excellent
Chemical resistance	Poor-Excellent	Moderate-Excellent
Permeability, H_2O	Very low-high	Very low
Gloss	Low-high	High-very high
Recoatability	Excellent	Poor-good
Low VOC use	Poor	Excellent

Film Formation

Some Milestones:

- A Film is dry-to-touch when viscosity is >10^3 Pa.s
- To resist blocking for 2s at 20 Psi, need viscosity >10^7 Pa.s
- To serve as industrial enamel, viscosity often must be >10^{12} Pa.s, the viscosity at Tg.





Film Formation

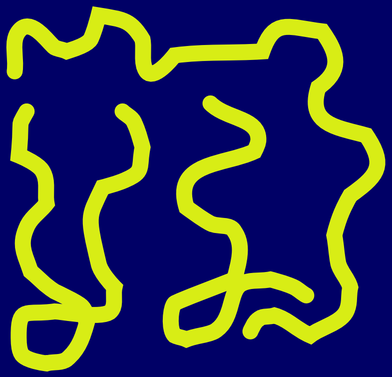
Relationship between viscosity and temperature

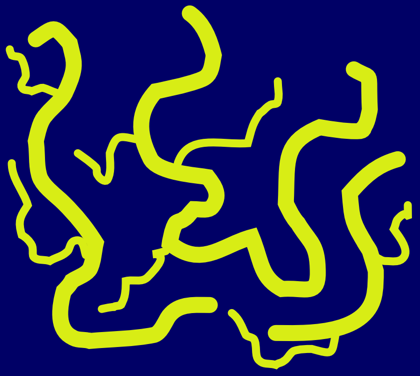
$$\ln? \quad = \quad 27.6 \; - \; \frac{40.2\,(T\text{-}Tg)}{51.6 \; + \; (T\text{-}Tg)}$$

T, in Kelvin-degrees

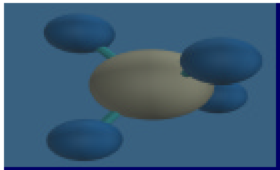
Williams, Landel and Ferry (WLF) Equation

Thermoplastic Systems


Linear and Soluble


Branched and Soluble

Polymer chains are longer but remain separate. Though they may coil around one another and exhibit branching, there is no primary valency bonding between chains.



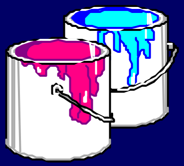
Thermoplastic Coatings

Film Formation by Evaporation of Solvent from Solutions of Polymers-- Lacquers

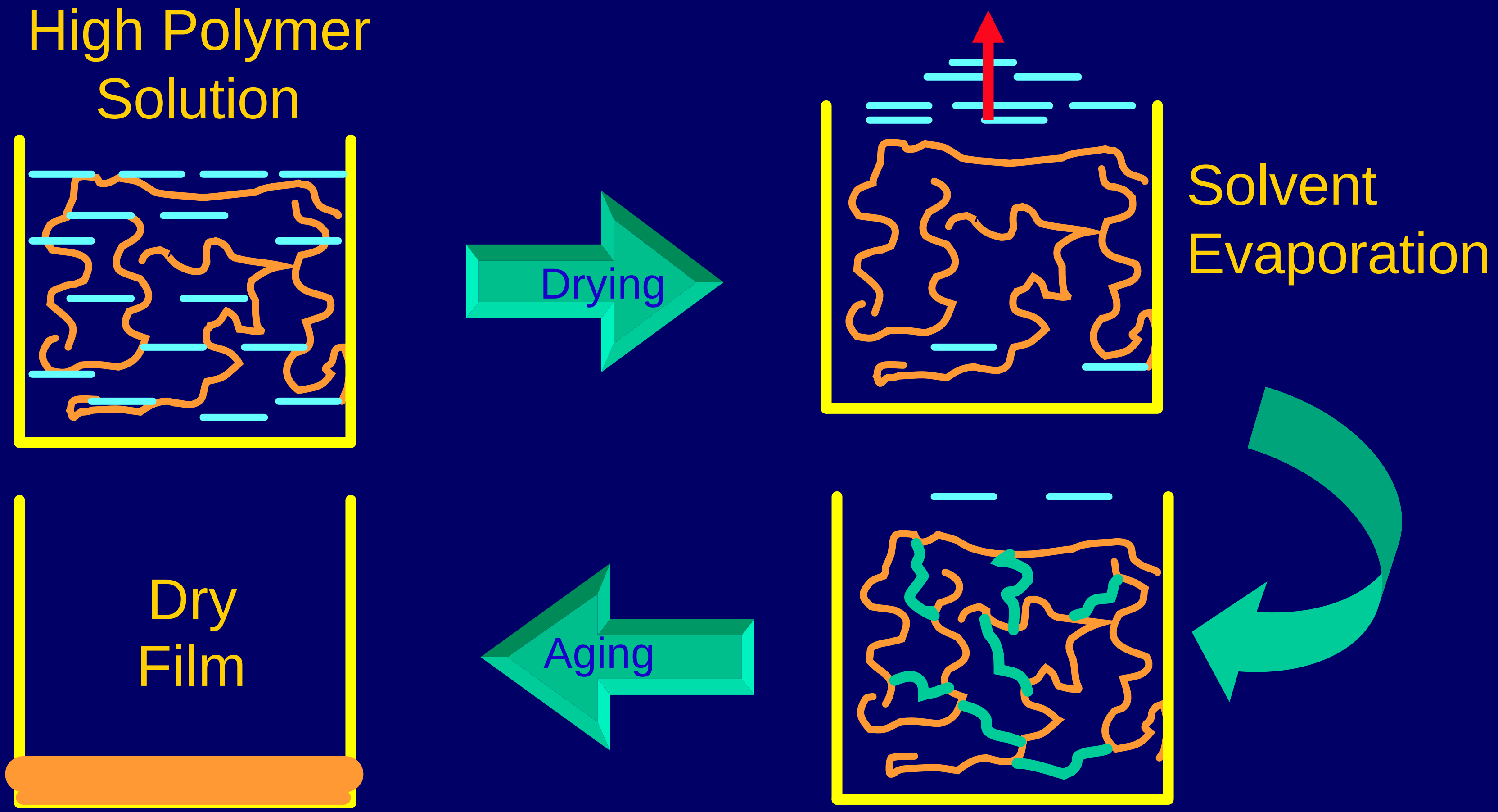
- **To have good film properties, polymer molecules must be large (very high molecular weight)**

However,

- **Concentrated solutions of high molecular weight polymers are too viscous. Dilute solutions have high VOC.**



Film Formation--Air dry (Lacquer)



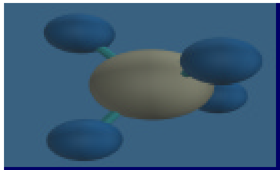
High Polymer Solution

Drying

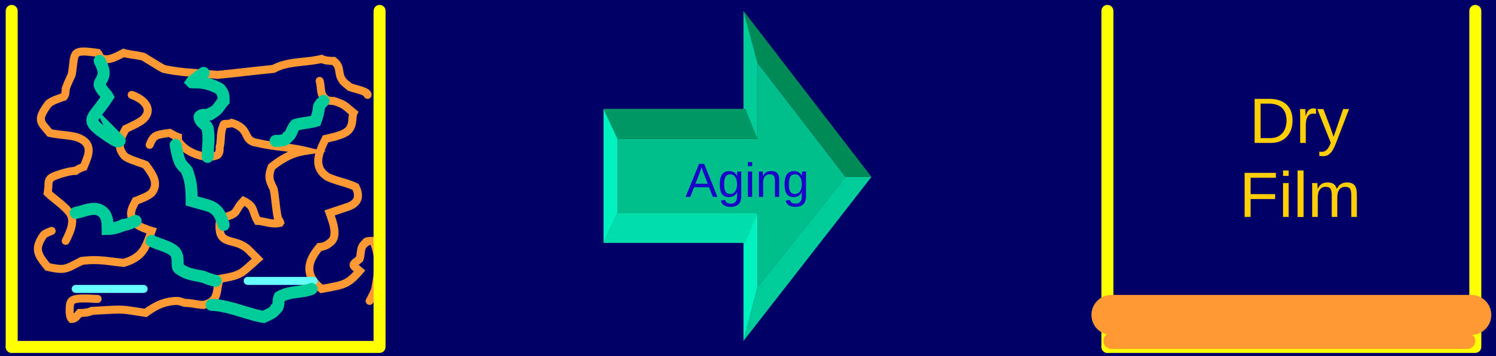
Solvent Evaporation

Aging

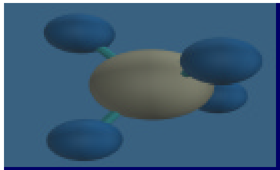
Dry Film



Film Formation--Air dry (Lacquer)



The cross chain linkages are weak secondary valency bonds broken relatively easily as the film is dissolved or melted



Principles of Film Formation

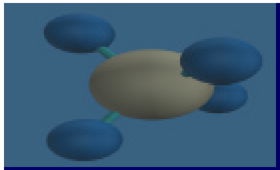
Stages of film formation (High T_g)

- At the early stages of drying, the rate of solvent evaporation is essentially independent of the presence of polymer
- The rate of evaporation depends upon

  -The vapor pressure

  -The ratio of surface area to volume of the film

  -The rate of air flow



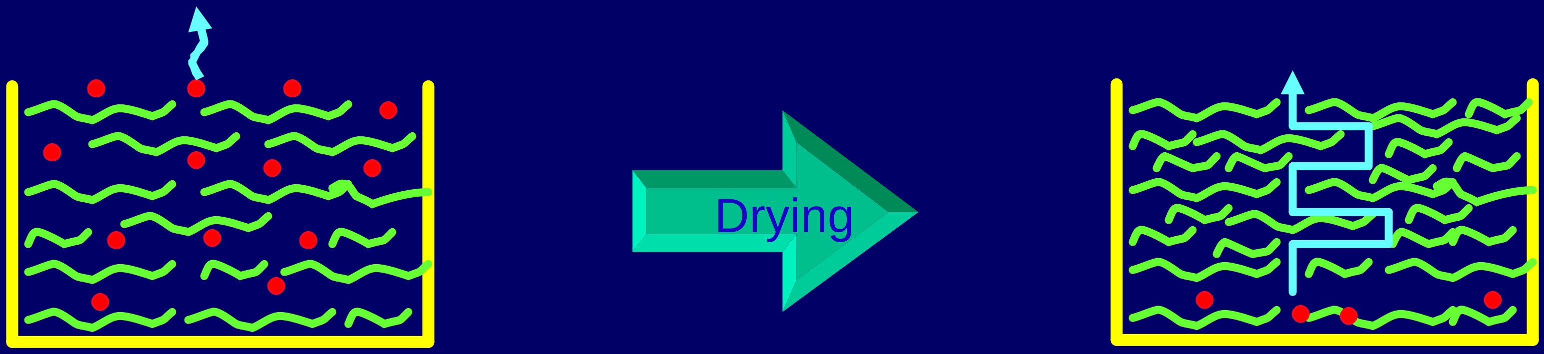
Principles of Film Formation

Stages of Film formation

As the viscosity and T_g increase, free volume decreases, and the rate of solvent evaporation depends on how rapidly the solvent molecules can reach the surface of the film.

The rate of solvent loss is controlled by the rate of *DIFFUSION* of the solvent through the film.

Principles of Film Formation



Lower T_g and more
free-volume available
Solvent evaporates easily

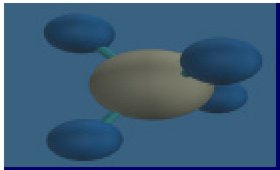
↓

Vapor pressure controlled

Higher T_g, and viscosity
Lower free volume

↓

Diffusion controlled



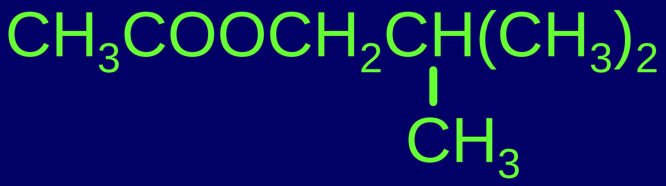
Film Formulation-Thermoplastic Polymers

The rate of solvent diffusion and evaporation also depends on the solvent structure and the solvent polymer interaction.

$CH_3COOCH_2(CH_2)_2CH_3$

n-Butyl acetate

Diffuses more rapidly



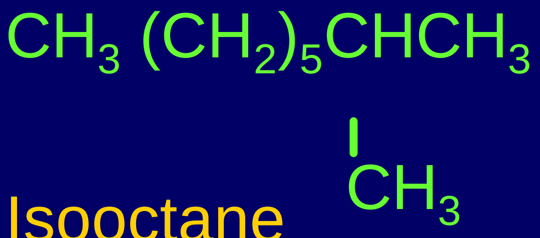
$CH_3COOCH_2CH(CH_3)_2$ with CH_3 on the CH

Isobutyl acetate

Higher evaporation rate

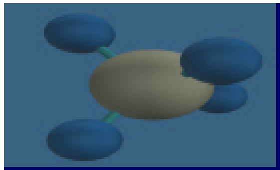
$CH_3\ (CH_2)_6CH_3$

n-Octane



$CH_3\ (CH_2)_5CHCH_3$ with CH_3 on the CH

Isooctane

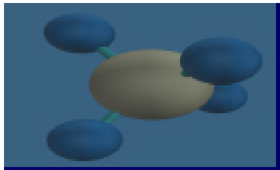


Thermoset Systems

Chemically reactive systems

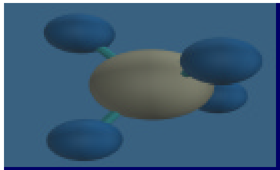
Main Resin	Cross-linker
Polyols	Amino Resins
Polyols	(Poly)isocyanates
Polycarboxylic acids	Epoxies
Polycarboxylic acids	Carbodiimides
Polycarboxylic acids	Aziridines
(Poly)amines, amides	Epoxies
Acetoacetate (active methylene)	Amino resins
Acetoacetate (active methylene)	(Poly)isocyanate
Polyols and polycarboxylic acids	Siloxanes

Miscellaneous Combinations



Thermoset Systems

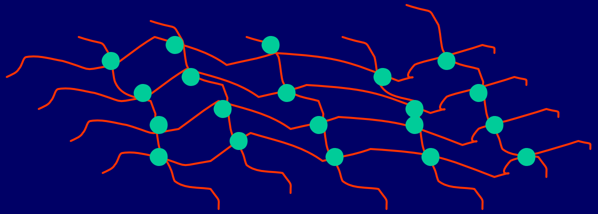
- The mechanical properties of the film depend strongly upon the T_g of the crosslinked polymer and upon the degree of crosslinking
- Physical properties such as water and oxygen permeability, solvent and chemical resistance are affected by the degree of crosslink density.



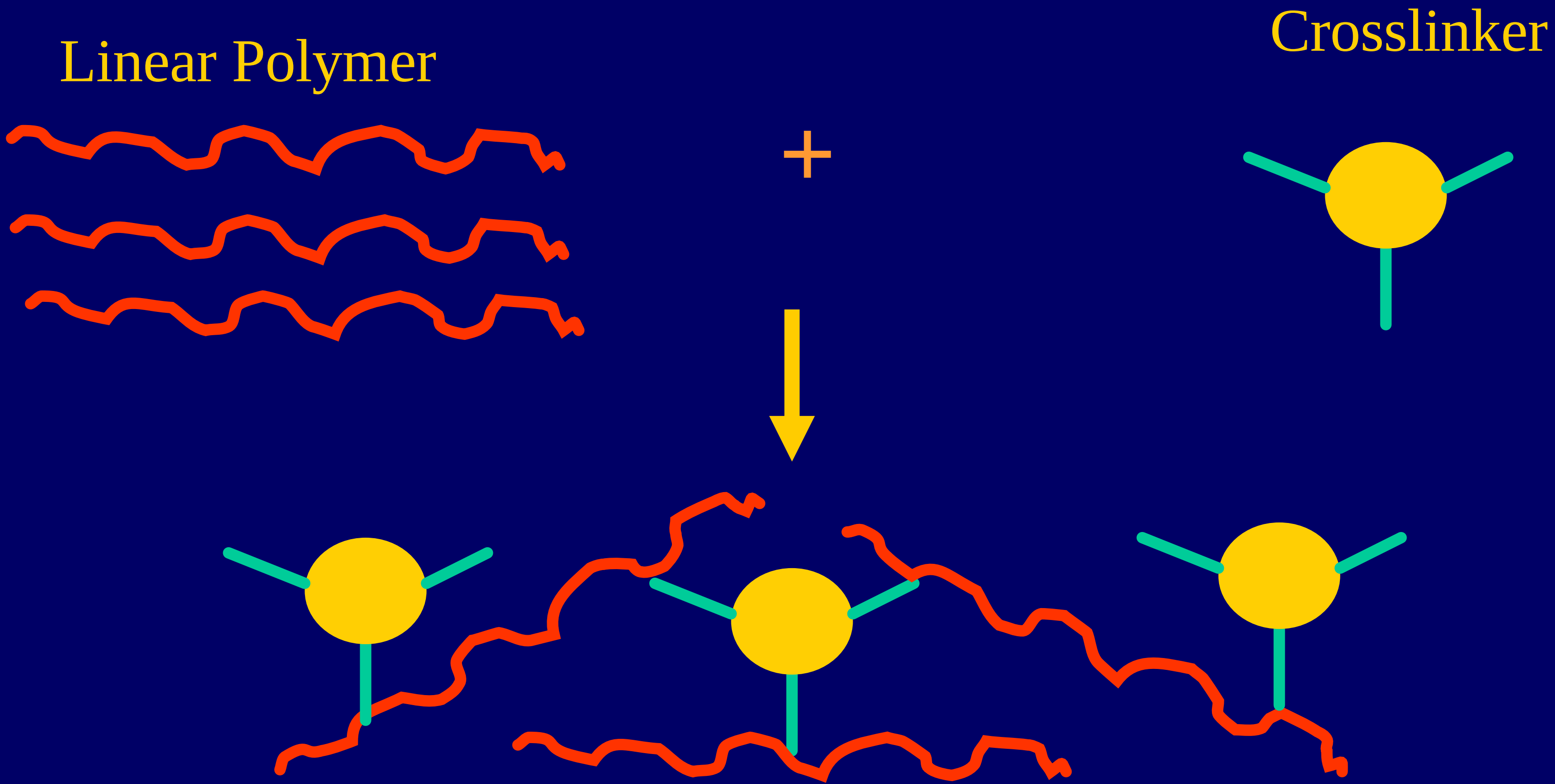
Crosslink Terminology

A number of extreme changes accompany crosslinking

Soluble → Insoluble
Flow → Severely reduced flow
Glass Transition Temperature → Increase in Tg



Crosslinking

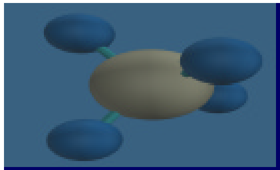


Linear Polymer

+

Crosslinker

Network (Crosslinked Polymer)



Thermoset Systems

T_g increases during crosslinking for three reasons:

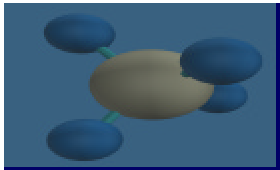
- Chain mobility near crosslinks is constrained
- Crosslinkers are converted from plasticizers to network chain segments
- M_n of main resin increases sharply

Thermoset Systems

Crosslinking requires that the reactants diffuse into a reaction volume

Small molecules may diffuse more readily than functional groups on a polymer chain

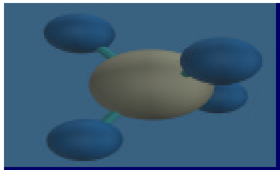
Water plasticizes coatings, lowering their Tg



Thermoset Systems

If the diffusion rate is greater than the reaction rate, the reaction will be kinetically controlled

If the diffusion rate is slow compared to the reaction rate, the rate is mobility controlled



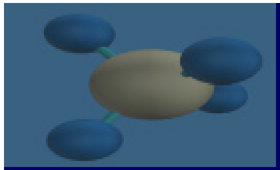
Thermoset Systems

The major factor controlling rate is the availability of free volume

The free volume is large if the reaction temperature is higher than the Tg

If the reaction temperature is below Tg, the free volume is limited

At intermediate temperatures, the reaction is controlled by the rate of diffusion *(mobility of reactants).*



Thermoset Systems

If the reaction temperature is above the Tg of fully reacted polymer, there will be no mobility effect

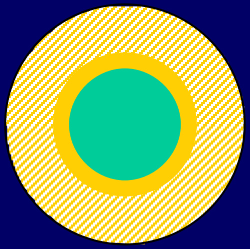
In ambient curing coatings if the Tg of the fully cured polymer is above the ambient, the reaction will become mobility controlled

As Tg approaches the cure temperature, reaction becomes slower

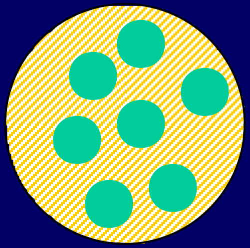
When Tg equals T, reactions become very slow and *Vitrification* occurs.

Film Formation in Latex Systems

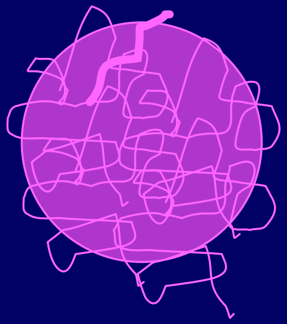
Film Formation--Waterborne Coatings



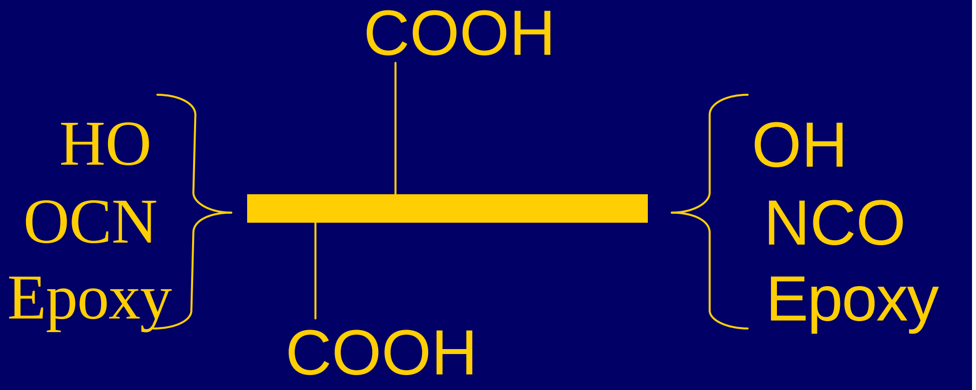
Core-Shell Latex



Multiphase Latex



Dispersion



COOH

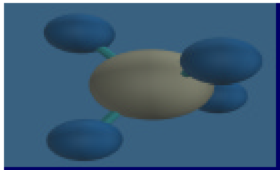
HO
OCN
Epoxy

OH
NCO
Epoxy

COOH

Epoxy
Alkyd
Acrylic
Polyester
Polyurethane

Resins



Film Formation from Latex

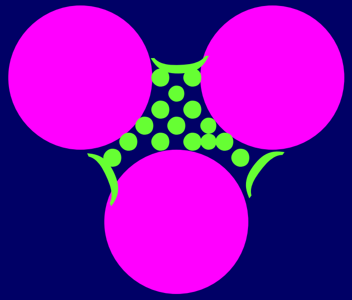
Occurs in three overlapping stages

- **Evaporation** of water and co-solvents leading to close packed layers of latex particles
- **Deformation** of the particles from their spherical shape leading to a more or less continuous layer
- **Coalescence**, a relatively slow process in which the polymer particles and molecules interdiffuse across the particle boundaries and tangle, strengthening the film.

Film Formation from Latex

What Derives Deformation?

- Capillary forces?
- Powerful (up to 5000 psi) but short lived
- Surface energy reduction?
- Much weaker but longer lived

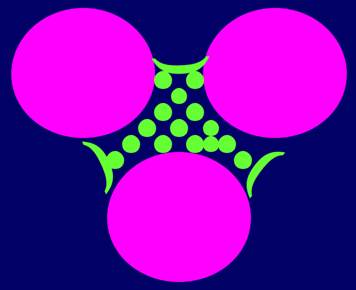


Film Formation from Latex

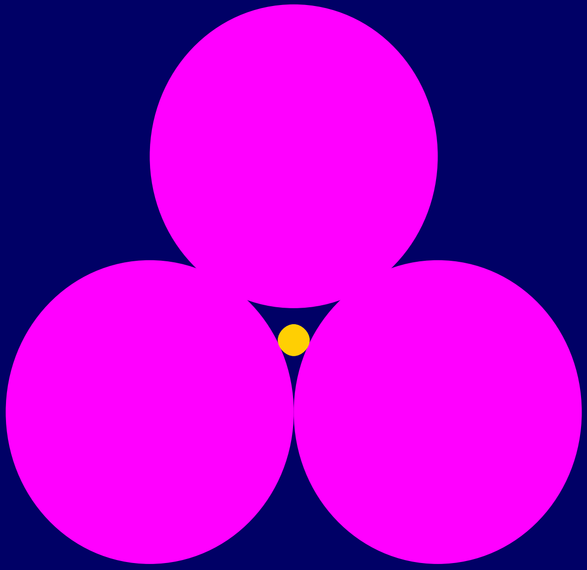
What Derives Deformation?

T_g of the latex particles is an important factor

- T_g of the outer shell is what counts
- particles and film can be plasticized by water and coalescent agents (solvents)

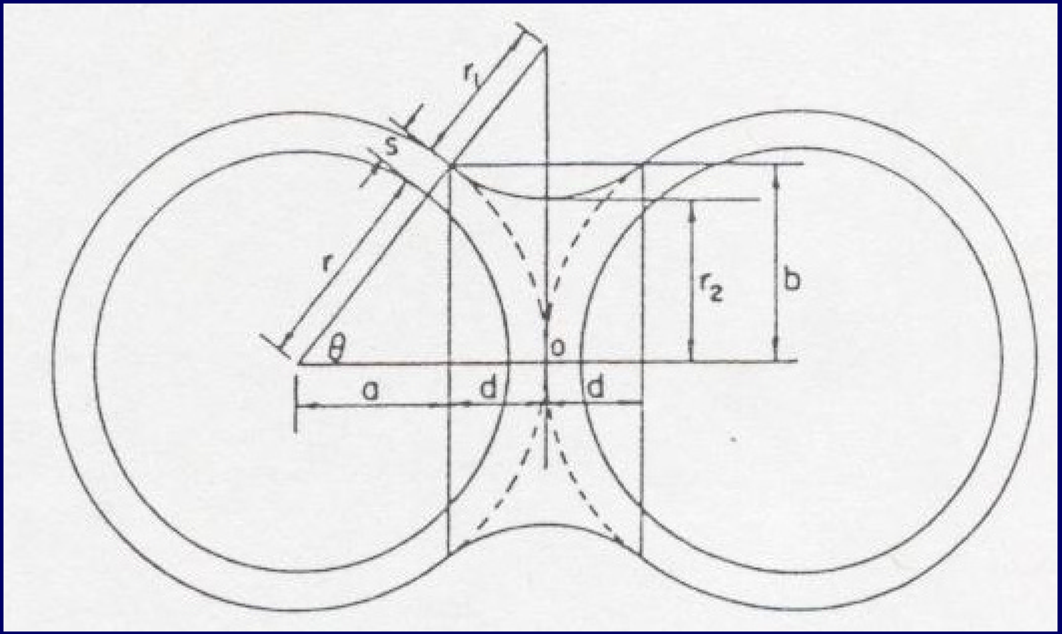


Film Formation



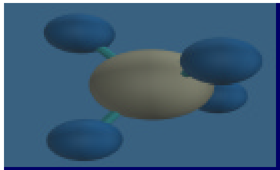
Top view of the drying latex showing three contacting particles with a capillary full of water in between

Film Formation



Thin layer of water around the particles

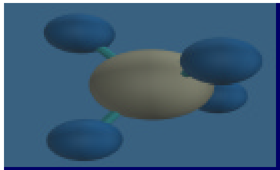
Schematic representation of two spheres in contact after partial evaporation of water



Coalescence

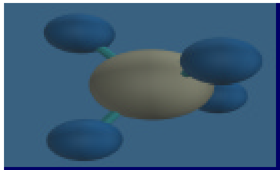
For a given latex, the lowest temperature at which coalescence occurs sufficiently to form a continuous cohesive film is called its

Minimum Film Formation Temperature **MM FT** (MFT)



Film Formation--Latex

- Complete coalescence is a slow process
- The rate is affected by $(T-T_g)$
- Coalescing agents reduce T_g and MFFT.

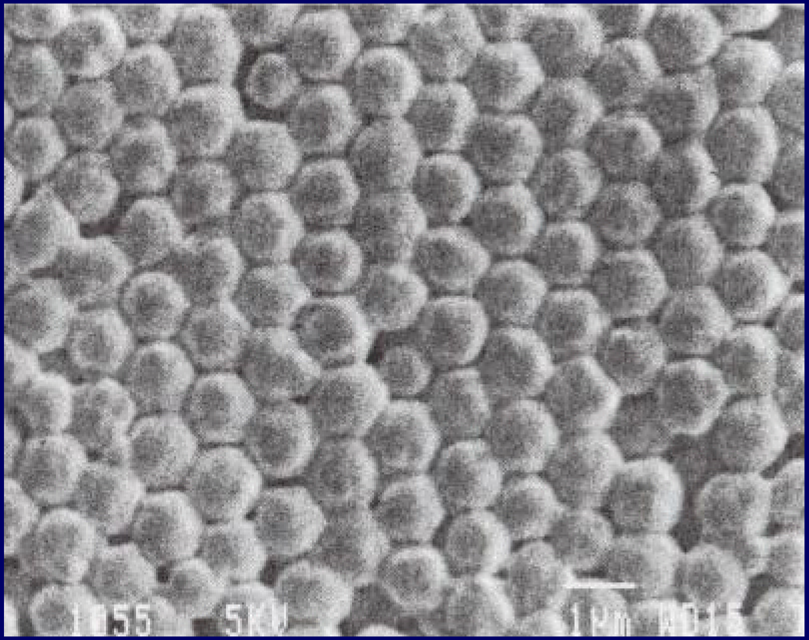


Coalescence

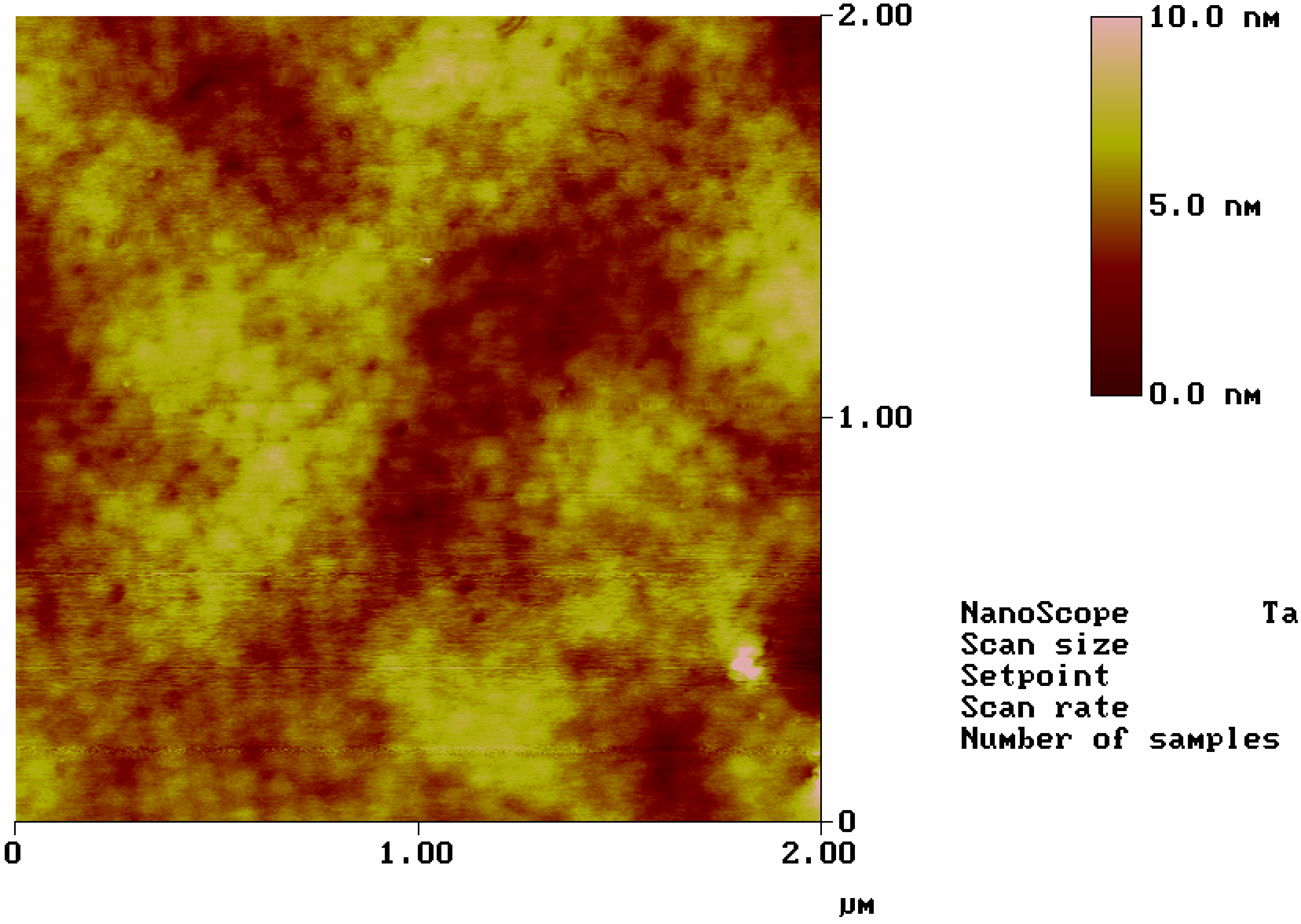
- Coalescence occurs as molecules interdiffuse. The distance the molecules travel to interdiffuse is considerably less than the diameter of a typical latex particle

- The rate of interdiffusion is directly related to $T\text{-}T_g$. As a broad rule, coalescence will not occur unless the temperature is at least slightly higher than T_g.

Film Formation



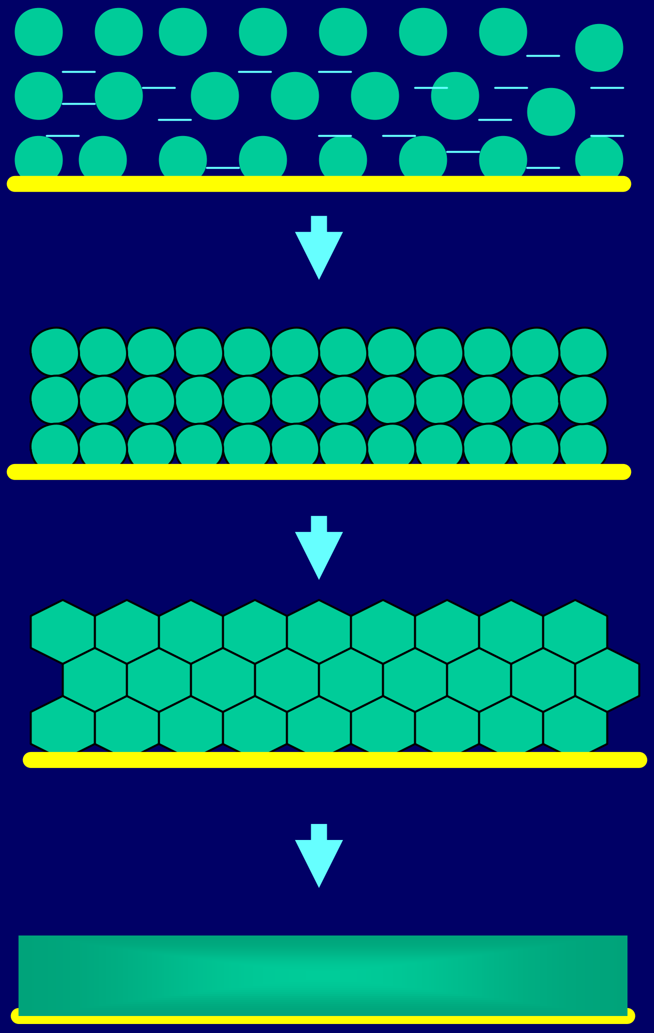
Scanning Electron Micrograph of films prepared from a latex polymer



NanoScope	Tapping AFM
Scan size	2.000
Setpoint	2.539
Scan rate	1.489
Number of samples	512

a.002

Latex Film Formation



Aqueous Latex

Stage I
Water Evaporation

Close-Contact
Particles

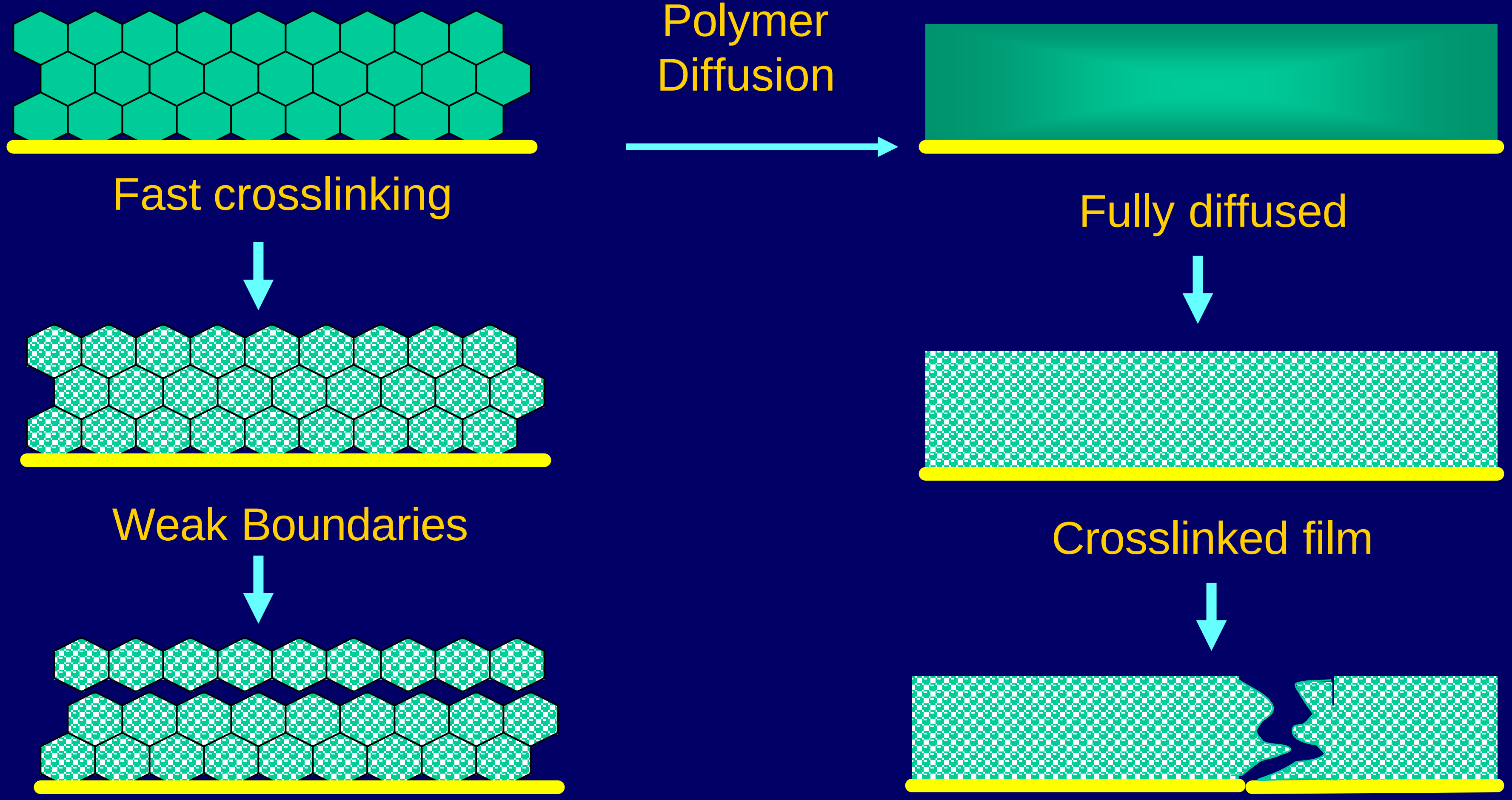
Stage II
Particles Deform

Packing of
Deformed Particles

Stage III
Coalescence (aging)

Mechanically
Coherent **Dry** Film

Crosslinking Latex



Fast crosslinking

Weak Boundaries

Weak film interfacial fracture

Polymer Diffusion

Fully diffused

Crosslinked film

Strong film cohesive fracture

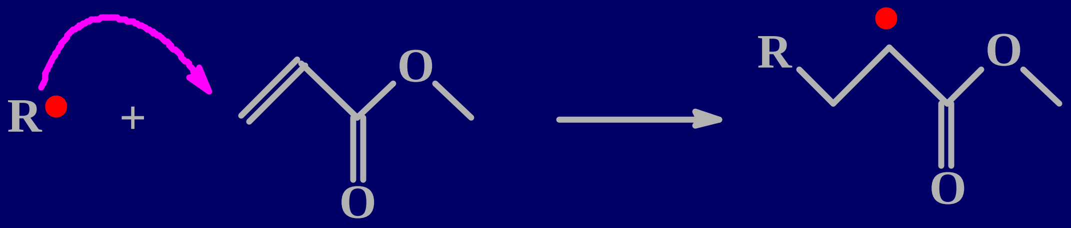
Film Formation in Energy Cured Coatings

“Energy ” Curing

- “Energy” Curing - initiation by:
  - UV: 200 - 400nm light
  - Visible: typically 380 - 450
  - Electron beam

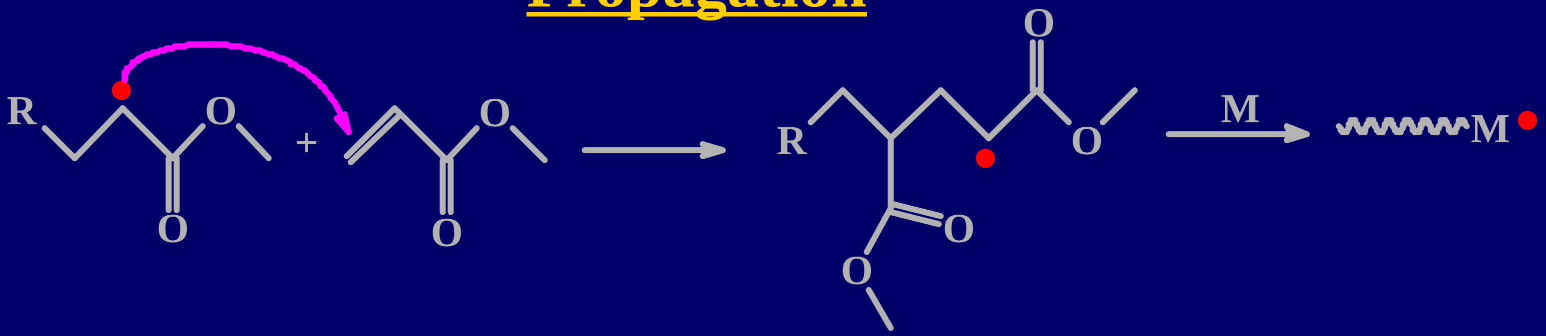
- Radical mechanism
- Cationic mechanism

Radical Curing Mechanism

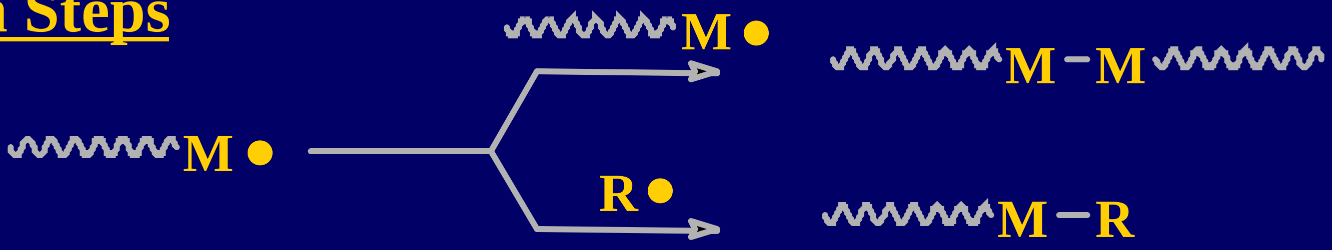


Initiation Step

Propagation



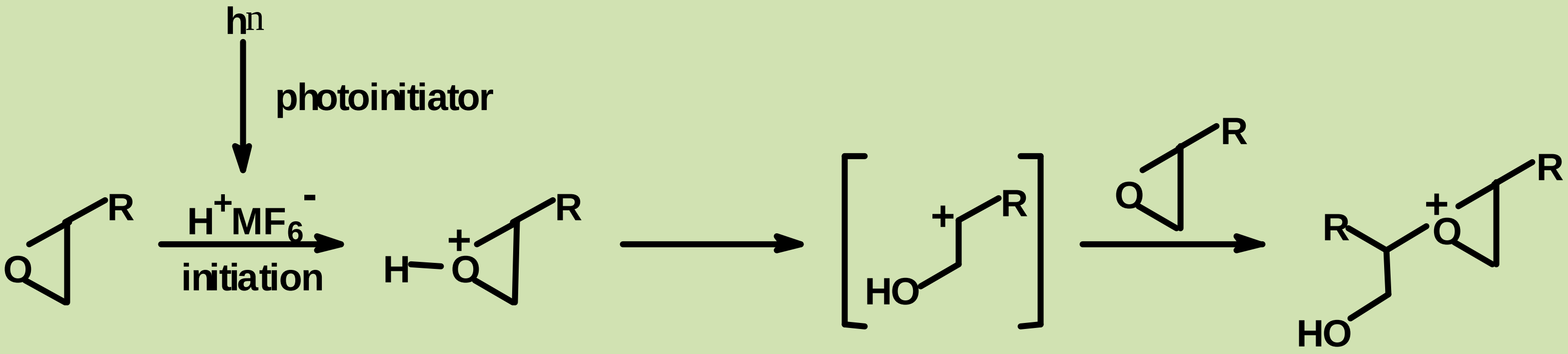
Termination Steps



Cationic Curing Mechanism

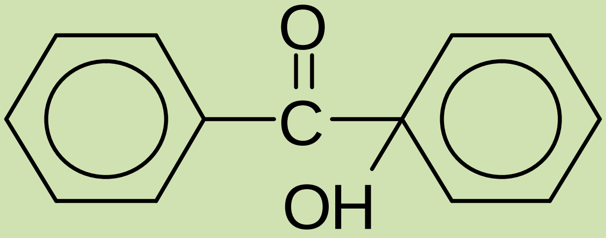
CATIONIC CURING - UV

Initiation (Light & Heat)

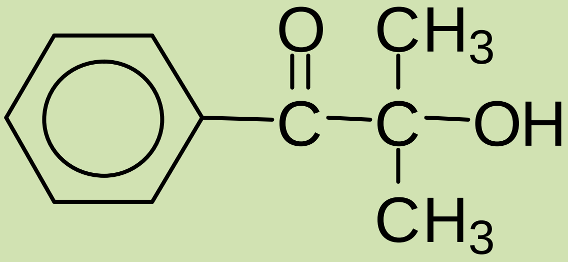


Common Photoinitiators

Photocleavage - Type I

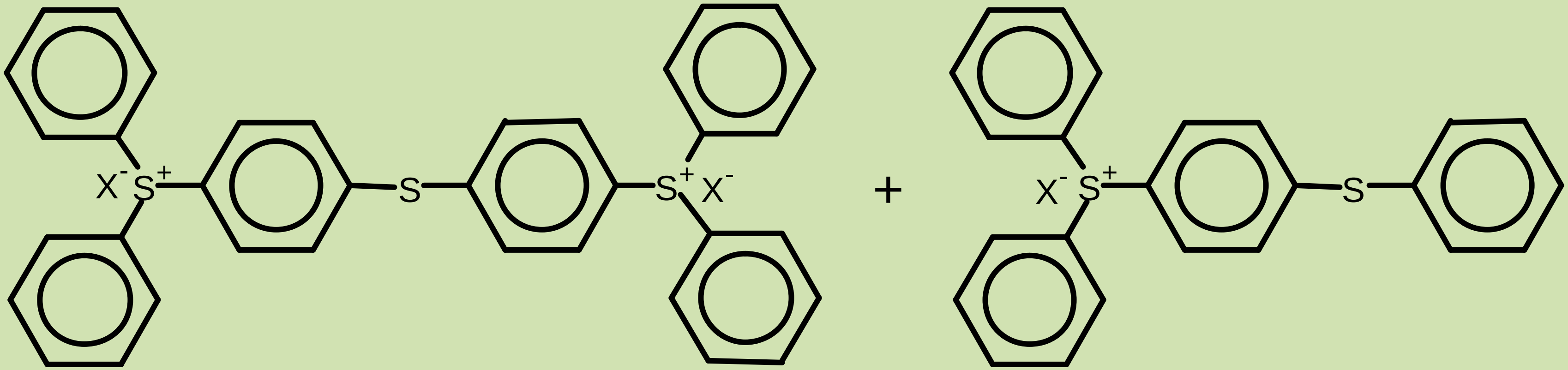


1-hydroxycyclohexyl phenyl ketone



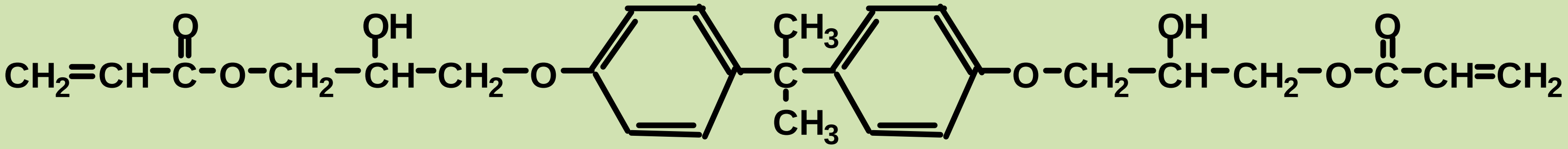
2-hydroxy-2-methyl-1-phenyl-propan-1-one

Sulphonium Salt Cationic Photoinitiators

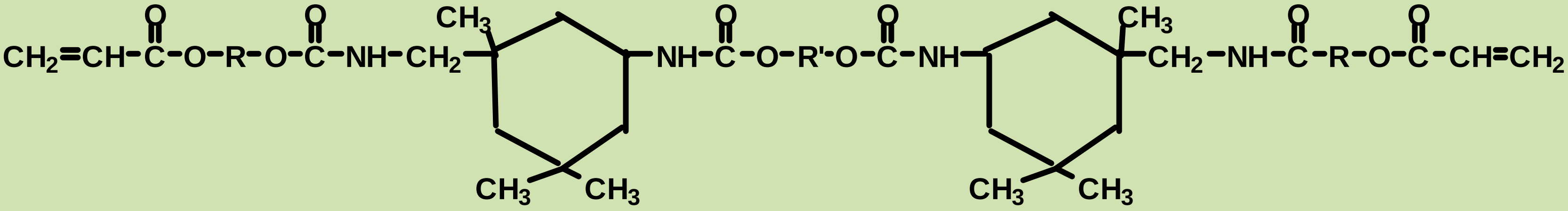


X = PF_6^- or SbF_6^- counterion

Oligomers



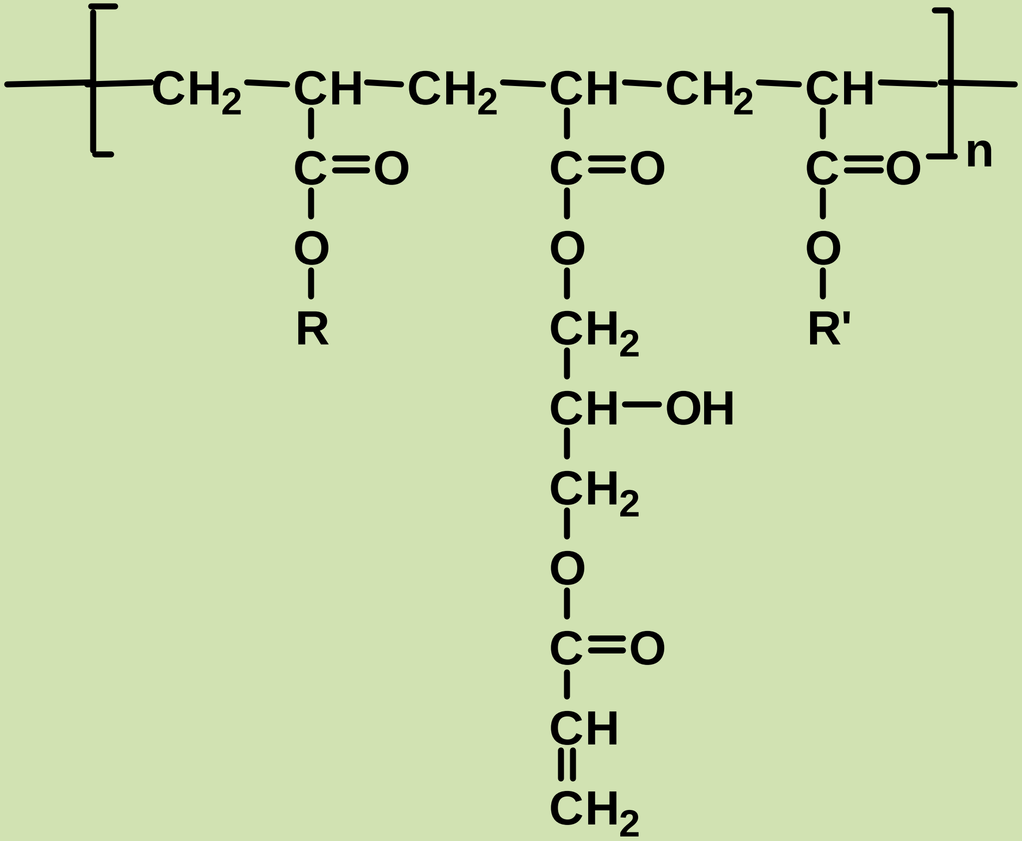
bisphenol A diglycidyl ether diacrylate



aliphatic urethane diacrylate

Oligomers

Acrylated Acrylic



Film Formation in Powder Coatings

Film Formation in Powder Coatings

There are two major classifications of powder coatings, Thermoplastic and Thermosetting.

Thermoplastic powders melt and flow with the application of heat.

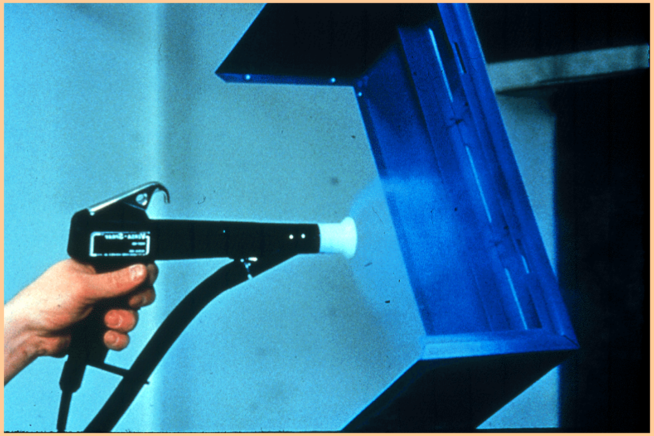
PVC, Nylon, Polypropylene, Vinyl, and Fluorinated resins

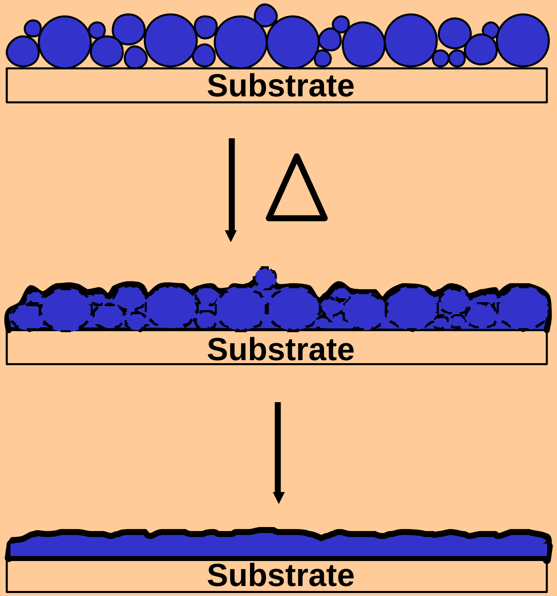
Thermosetting powders

Epoxy, polyester, polyurethane, and acrylic and combinations thereof.

POWDER COATING

A finely ground mixture of ingredients in a resinous base, which are solid at the time of application, but melt, flow, and coalesce into a protective film in the presence of heat.





Substrate

Δ

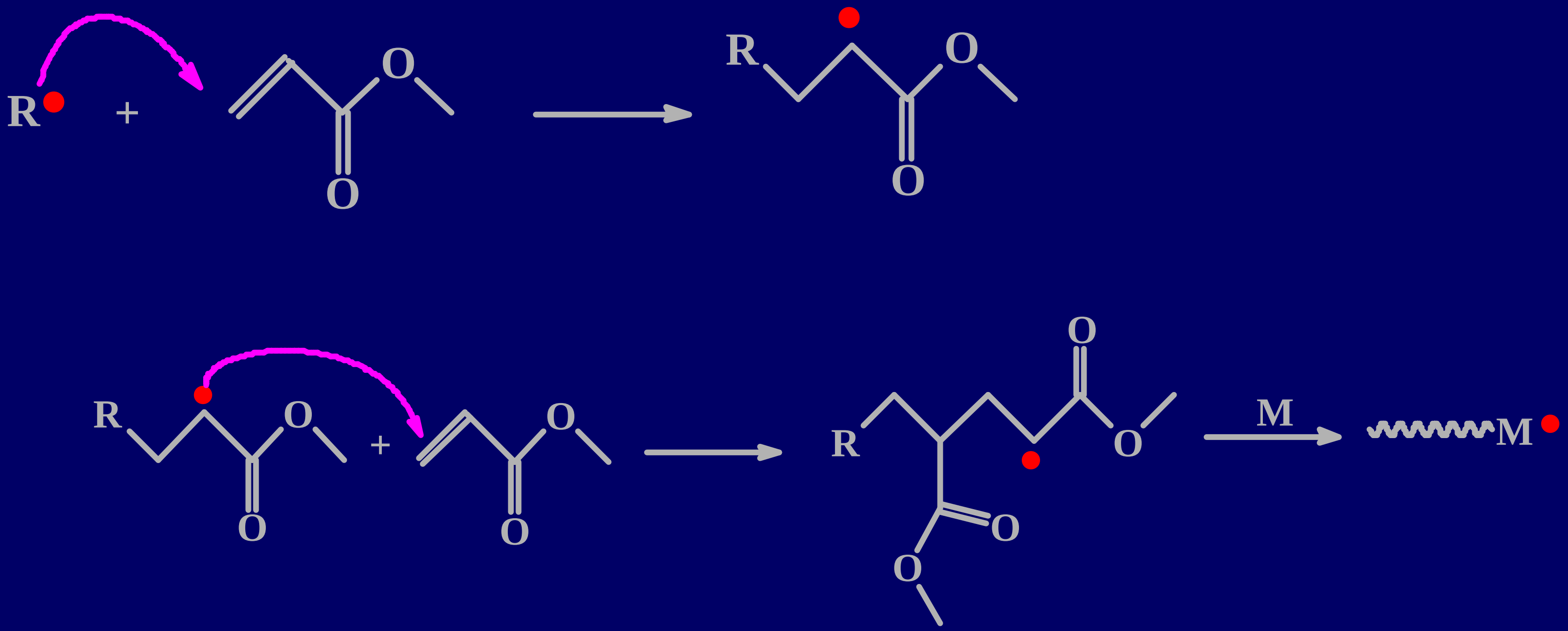
melting

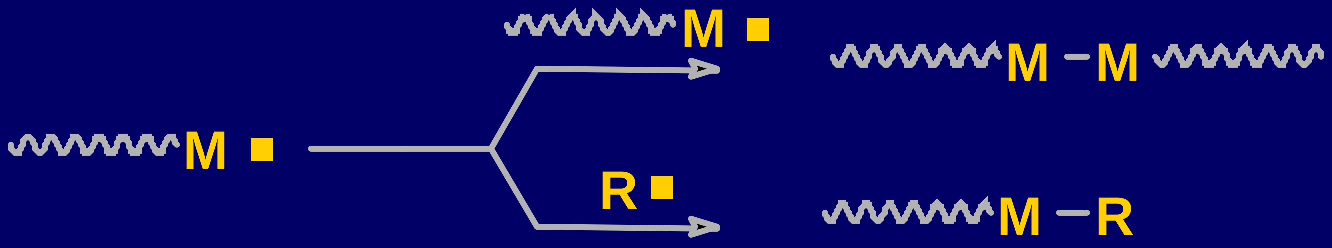
Substrate

leveling/curing

Substrate

Radical Curing Powder Coating





UV Cured Powder

- These powders follow a combination of conventional and UV cured systems.

- The melt and low is accomplished by a brief exposure to a heat source

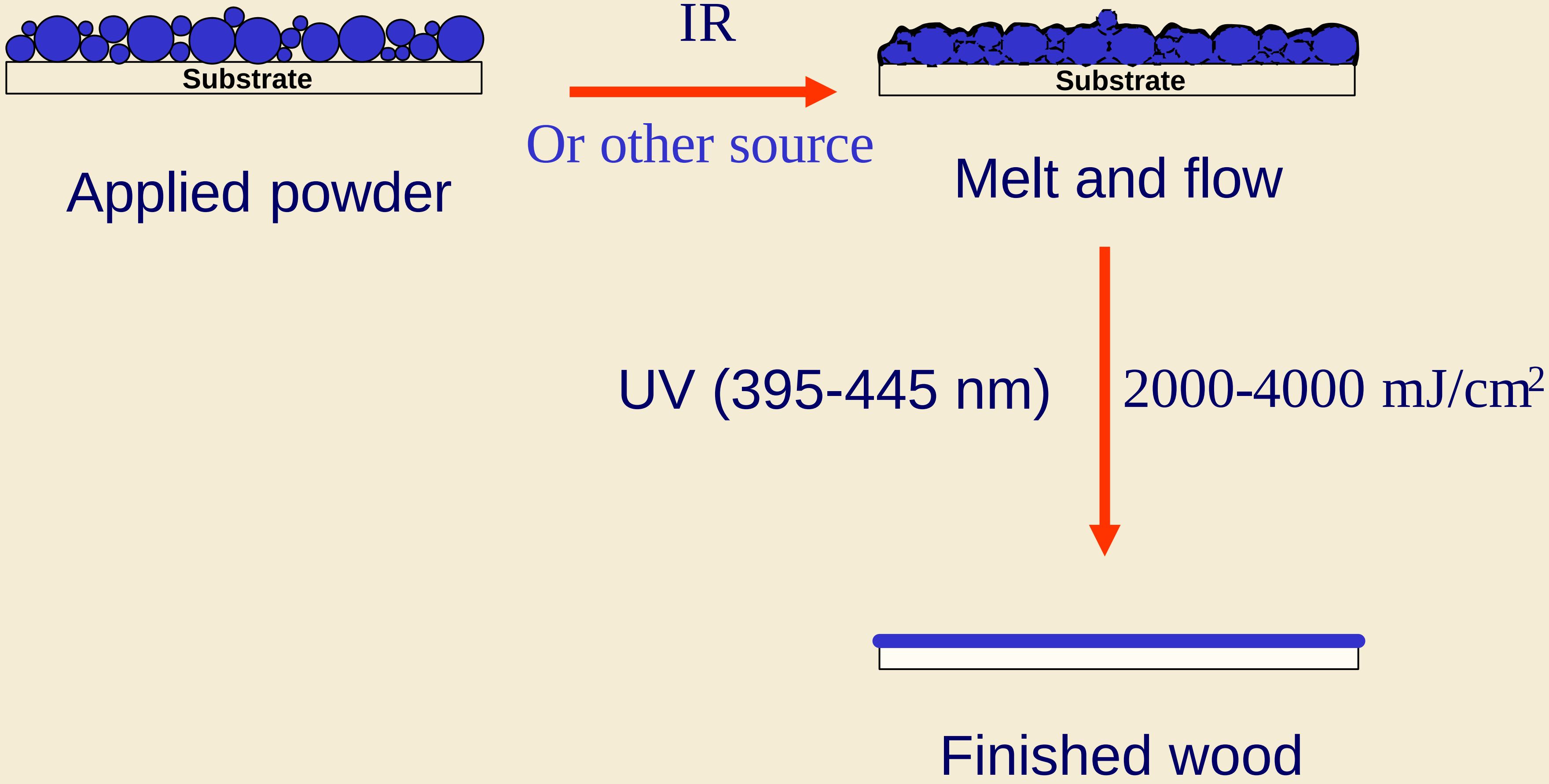
- The cure and cross linking is achieved by a brief exposure to an ultraviolet light source.

This technology is suitable for powder coating temperature sensitive materials such as wood products (MDF)

Challenges

- Highly pigmented systems are slow to cure
- Film thickness limitations
- Balance of good flow and cure is critical
- Line-of-Site

Film Formation



Applied powder

IR

Or other source

Melt and flow

UV (395-445 nm)

2000-4000 mJ/cm^2

Finished wood

Film Formation in Coatings

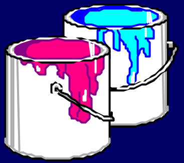
References

Organic Coatings: Science and Technology, Z., Wicks, F., Jones, P. Pappas, John Wiley and Sons, 1999.

Protective Coatings: Fundamentals of Chemistry and Composition, C. H. Hare, Technology Publishing Company, 1994.

Adhesion Aspects of Polymeric Coatings, J. Baghdachi, FSCT, 1997

Waterborne Coatings: A compilation of Papers from the Journal of Coatings Technology, 2001



Thank You!